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ANALYSIS OF SILICATE ROCKS
PART 1 : ROUTINE DETERMINATION OF
MAJOR CONSTITUENTS

by

T. Rigg and H. A. Wagenbauer



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Preliminary Report 64-1

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PART I: ROUTINE DETERMINATION OF
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T. Rigg and H. A. Wagenbauer

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ANALYSIS OF SILICATE ROCKS

PART I: ROUTINE DETERMINATION OF MAJOR CONSTITUENTS

Abstract

The analytical methods described in this report are those used in the Chemistry Laboratory of the Geology Division of the Research Council of Alberta for the routine analysis of silicate rocks. Methods are given for the determination of SiO_2 , Al_2O_3 , Fe_2O_3 , FeO , MgO , CaO , Na_2O , K_2O , loss on ignition, TiO_2 , P_2O_5 and MnO . All of the methods have been chosen on the basis of maximum rapidity and convenience consistent with adequate reliability. Included are the results of applying the methods to the analysis of U.S. Geological Survey Samples G-1 and W-1. The sources of error in the various individual determinations and the reliability of the analytical system as a whole are discussed.

INTRODUCTION

The solutions of many problems arising in the course of geological studies are often and unavoidably based on chemical analyses. Obviously, if the chemical analyses are not sufficiently accurate and reliable, the geological conclusions based upon them must have limited value. Extreme accuracy in chemical analysis can be obtained only by highly skilled operators using refined techniques which are necessarily very time-consuming. In a relatively small laboratory where chemical analyses are dealt with as a service to geologists, some compromise between speed and accuracy must be reached if an adequate number of analyses is to be turned out.

A number of schemes for the rapid analysis of silicate rocks have been proposed, as for example by Shapiro and Brannock (1956), but after trials of such methods in the Research Council rock-analysis laboratory it has been concluded that they offer inadequate accuracy for most geological purposes. The most unsatisfactory features of the "rapid" analytical schemes are colorimetric methods for silica and alumina and complexometric methods for calcium. These methods have been avoided in the analytical scheme described in the following pages. Directions are given for carrying out analysis for all major constituents of silicate rocks by methods which have been found to offer the best compromise between operating time and complexity on the one hand and accuracy, precision and freedom from interferences on the other.

This publication is intended to serve as a guide for those engaged in the routine determination of the major constituents of silicate rocks and

to preserve in permanent form the methods arrived at as a result of several years experience of this type of analysis. It is also intended for the information of those individuals and organizations submitting samples to, or co-operating with, the Research Council laboratory.

It should be noted that to obtain optimum results it is essential to follow the directions closely. The directions are particularly intended for the analysis of igneous rocks, but will generally be found quite suitable for other silicate rocks of sedimentary or metamorphic type.

ROCK COMPOSITION

Table 1 shows the average composition (cf. Mason, 1958) of the earth's crust, about 95 per cent of which is comprised of igneous rocks. Oxides of the first eight elements listed together comprise about 98 per cent of the total mass of the crust. In addition to these elements, almost all igneous rocks contain small amounts of titanium, phosphorus and manganese. The percentages of the most important constituents usually lie within the following ranges: SiO_2 , 35-80; Al_2O_3 , 10-22; Fe_2O_3 , 1-10; FeO , 1-12; MgO , 1-12; CaO , 1-15; Na_2O , 2-5; K_2O , 1-6. The water content of igneous rocks is generally less than 2 per cent, although the amount present in some volcanic glasses may be as high as 10 per cent.

The present work deals only with analyses for the major constituents of silicate rocks as defined originally by Washington (1930): SiO_2 , Al_2O_3 , Fe_2O_3 , FeO , MgO , CaO , Na_2O , K_2O , $\text{H}_2\text{O}+$ ($>110^\circ$), $\text{H}_2\text{O}-$ ($<110^\circ$), TiO_2 , P_2O_5 , MnO .

OUTLINE OF ANALYTICAL SYSTEM

A sample of the rock is fused with sodium carbonate and taken into solution in dilute hydrochloric acid. After separation of the silica, the "mixed oxides" are precipitated with ammonia and filtered off. Calcium in the filtrate is determined volumetrically as oxalate, then magnesium is determined by complexometric titration using Versene (di-sodium salt of ethylenediamine tetra-acetic acid) and Eriochrome Black T.

A second solution of the rock is prepared by digesting a sample with a mixture of hydrofluoric and sulfuric acids. This solution is used for the spectrophotometric determination of total iron, titanium, phosphorus and manganese, the instructions given being particularly suited to the use of 2.5-centimetre diameter test tubes in a Beckman type B spectrophotometer. The amounts of sodium and potassium in this solution are measured with a flame photometer. A further separate rock sample is digested with hydrofluoric acid and sulfuric acid for the determination of the ferrous iron content by permanganometric titration. Hygroscopic water

Table 1. Average Composition of the Earth's Crust

| Constituent | Percentage | Constituent | Percentage |
|-------------------------------------|---------------|--------------------------------|------------|
| SiO ₂ | 59.35 | SrO | 0.036 |
| Al ₂ O ₃ | 15.37 | Rb ₂ O | 0.034 |
| Fe ₂ O ₃ /FeO | 6.43 (as FeO) | F | 0.03 |
| CaO | 5.08 | Cl | 0.03 |
| Na ₂ O | 3.82 | ZrO ₂ | 0.030 |
| MgO | 3.47 | Cr ₂ O ₃ | 0.029 |
| K ₂ O | 3.12 | BaO | 0.028 |
| H ₂ O | 1.26 | V ₂ O ₃ | 0.022 |
| TiO ₂ | 0.74 | ZnO | 0.016 |
| P ₂ O ₅ | 0.27 | Li ₂ O | 0.014 |
| MnO | 0.13 | CuO | 0.012 |
| CO ₂ | 0.12 | NiO | 0.012 |
| S | 0.052 | WO ₃ | 0.01 |

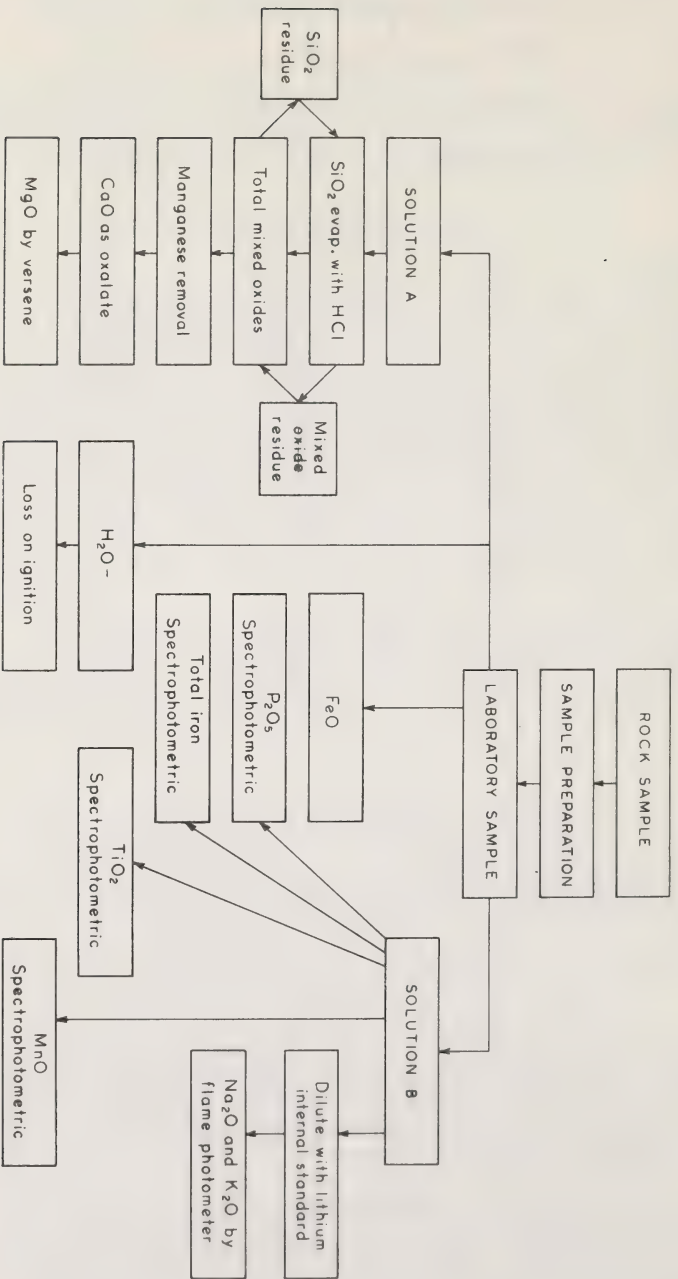
is determined as the loss in weight on drying, while chemically bound water is not determined specifically but is included in, and is largely responsible for, the loss of weight on ignition. The block diagram shown in figure 1 illustrates the system schematically.

ANALYTICAL METHODS

The analytical methods are outlined in the order of consecutive determinations as shown in the schematic block diagram (Fig. 1). For the sake of brevity, and to facilitate use by Research Council staff or others who may wish to follow the procedures, the methods are set out in the form of a laboratory manual.

The outline does not show the efficient utilization of equipment or the time gained by performing several determinations concurrently. In practice it is found that a batch of eight samples can be analyzed with little more effort than the analysis of a single sample. Delays while

FIGURE 1: PROCEDURE FOR ROUTINE CHEMICAL ANALYSIS OF SILICATE ROCKS



evaporating, heating, or igniting are inevitable, but frequently offer opportunities to begin or complete other parts of the analytical procedure. Evaporations and other time-consuming steps should be started in the late afternoon wherever possible so that hot plates, steam baths, fume hoods, etc., may be utilized overnight if constant supervision by the analyst is not required. It should be possible for an experienced analyst to process a batch of eight samples in ten to fourteen days provided that no unusual problems arise.

(1) Sample Preparation

Ten to one hundred grams (gm.) of rock sample — already broken or in a single piece provided that none of its dimensions exceed about 2 inches — should be placed between two pistons in a steel cylinder and crushed by forcing the pistons together.

The apparatus used in this laboratory (Fig. 2) was developed by J. D. Godfrey and consists of a hardened steel cylinder about 4 inches tall and 3 inches in diameter. The base piston is approximately 1 inch thick and the length of the ramming piston is about 5 inches. The pistons are of solid steel, oil-hardened after being machined to a very close but free-sliding fit in the cylinder. Both pistons are faced with 1/4 inch of tungsten carbide to prevent iron contamination of the samples. Crushing forces of up to 30 tons are applied to the ramming piston by means of a hydraulic press (Fig. 3).

The crushed rock should be sieved through a 16-mesh screen placed above a 100-mesh screen. The material retained by the coarse screen is first crushed until it all passes through onto the fine screen, then the material retained on the fine screen is crushed again until it all passes through the 100-mesh screen. The screens should preferably be made from nylon as metal ones can only be used when it is not intended to examine the rock for the metals of which the screens are composed. The minus 100-mesh powder must be well mixed and stored in a closed bottle. Sample splitting is carried out by the usual cone and quarter method.

Rock samples must never be ground in porcelain mortars, but the last remaining coarse material which is not enough to be dealt with easily in the hydraulic crusher may be ground to the required fineness in a "Diamonite" mortar. These are made from synthetic sapphire having a hardness of about 9 on Moh's scale, compared with 6 or 7 for agate. Ultra-fine grinding is not advisable on account of the risk of oxidation of FeO by atmospheric oxygen. Figure 2 shows the sample crushing and grinding equipment; figure 3 shows the sample crusher in use.

(2) Hygroscopic Water (H₂O-)

Weigh 1.0 gm. of sample into a platinum crucible. Heat the crucible and its contents in an air oven at 110° C for one-half hour and

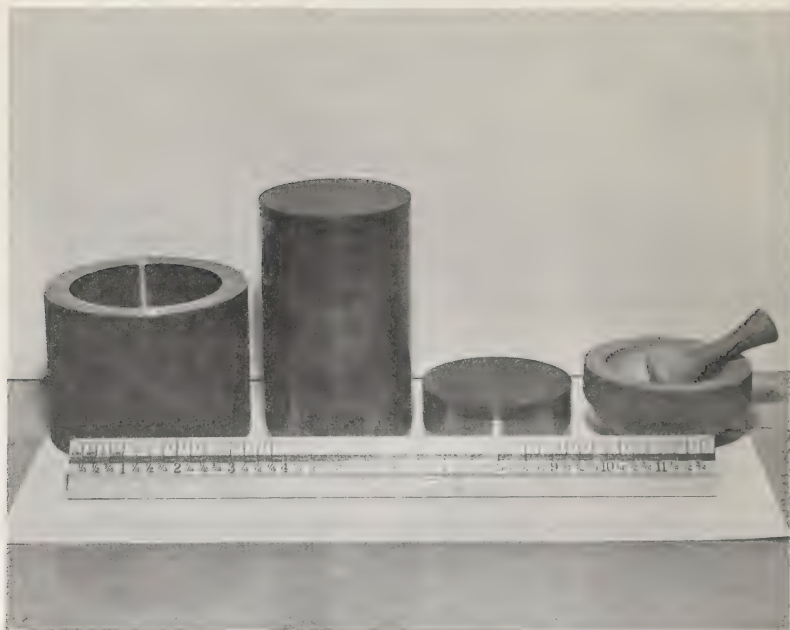


Figure 2. Sample crushing and grinding equipment. Alberta Government photograph.

allow to cool in a desiccator before reweighing. The heating should be continued for half-hour periods until constant weight is attained. Retain the dried sample for determination of the loss on ignition.

(3) Loss on Ignition (H_2O , CO_2 , etc.)

In this system of analysis the combined water is not determined as such. It should be noted that although the weight loss on ignition includes the loss of carbon dioxide from carbonate decomposition together with the loss of other less common volatile constituents, it is considered to give a sufficient indication of the water content for present purposes as carbon dioxide is generally regarded as only a minor component of silicate rocks.

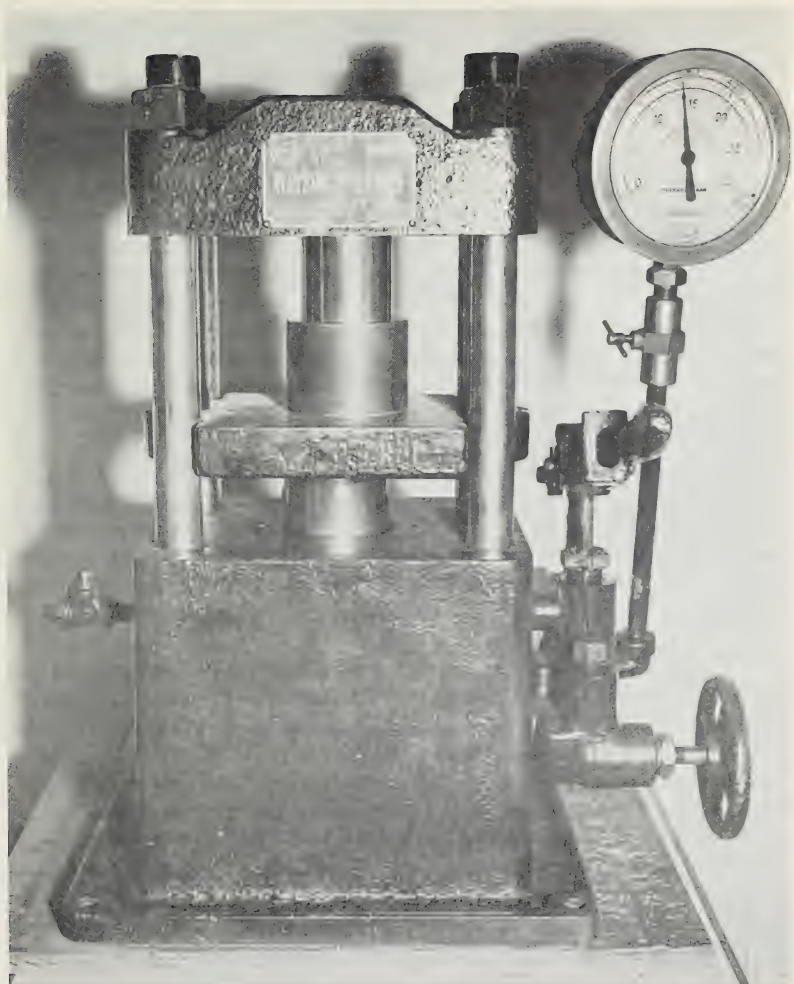


Figure 3. Sample crusher in use. Alberta Government photograph

Heat the crucible containing the 1.0-gm. sample used for the determination of hygroscopic water for one hour in an electric muffle furnace at $1150\text{--}1200^{\circ}\text{C}$, cool in a desiccator and reweigh. Repeat the heating for half-hour periods until constant weight is attained. The residue should be non-magnetic on testing with an "Alnico" or other powerful permanent magnet held against the outside of the crucible. The error arising from the oxidation of FeO to Fe_2O_3 is compensated for by adding algebraically 0.111 times the percentage of FeO in the dried sample to the observed percentage loss on ignition. Note that the "loss" may sometimes

become negative if the FeO content is large.

(4) Preparation of Solution A

If only a small amount of sample is available, or if sintering has not occurred, use the 1.0-gm. sample previously employed in determining the loss on ignition; otherwise weigh out a fresh 1.0-gm. sample into a platinum crucible. Add 5 to 6 gm. of analytical-grade anhydrous sodium carbonate to serve as a flux. Mix the sample and flux together using a piece of thin polyethylene rod as a stirrer, then cover the mixture with a thin layer of flux. Sample particles adhering to the stirring rod should be wiped off in this flux layer. Place the lid on the crucible and fuse over a Meker burner. The crucible should be brought up slowly to a bright red heat and this maintained until the whole mass in the crucible becomes fluid and no further evolution of carbon dioxide is evident. This usually requires about one-half hour, but this time may be shortened if the contents of the crucible are mixed by gentle swirling after fusion has occurred (Piper, 1950). When the decomposition is complete, remove the crucible from the burner and allow it to cool. Remove and heat the lid of the crucible strongly to melt any sodium carbonate that may have splashed onto it, thus making sure that any adhering rock particles are decomposed. Replace the lid on the crucible and allow both to cool.

Put the crucible lid in a 400-millilitre (ml.) Teflon* evaporating dish and add sufficient hot water to dissolve any of the melt that may be sticking to it. When the melt has dissolved from the cover remove it and rinse, wiping it with a small piece of Whatman No. 54 filter paper to ensure complete removal of the last traces of silica. Place the piece of filter paper in the dish and pour a small amount of the wash water on to the fused cake in the platinum crucible. Allow the crucible to stand for about one-half hour before returning the water and the disintegrated cake to the Teflon dish, washing the crucible as well as possible. If the cake proves to be difficult to dislodge, drain the crucible into the Teflon dish then heat it rapidly to about 400° C and immediately plunge it for two thirds of its depth into cold water. Repeat this treatment until the disintegrated cake can be removed without distortion of the crucible.

* Note on the use of Teflon evaporating dishes

Teflon is a trade name for polytetrafluoroethylene. Dishes made from this material have been in continuous service for analytical evaporations in the Research Council laboratory for two years. They are found to be greatly superior to silicate-based materials such as glass or porcelain, especially for the determination of silica by evaporating with hydrochloric acid. The material is inert, not wetted by the solutions, and the dehydrated silica is extremely easily removed from the surface of the dish. In general use it has been found that surface stains are readily removed from the dishes, without damaging the surface, by gently rubbing with a mildly abrasive household cleanser.

Use a polyethylene rod to scrub any firmly held portions of the fused cake from the crucible. Add 25 to 30 ml. of dilute hydrochloric acid (1 + 1) to the solution in the dish and immediately cover the dish with a ribbed watch glass to avoid losses due to effervescence. Pour 5 ml. of the dilute acid into the crucible to dissolve the last traces of the fusion residue. When the effervescence has ceased, rinse the watch glass into the Teflon dish and add the acid rinse from the crucible. The crucible should finally be rinsed with water and cleaned out with a small piece of No. 54 filter paper which should be added to the contents of the dish. The solution A thus prepared should have a volume of about 100 ml. and should be clear except perhaps for a certain amount of silica floc. There must be no sign of unattacked rock particles.

(5) Determination of SiO_2

Place the Teflon dish on a steam bath and evaporate the contents to dryness. To make sure that the dehydration of the silica is complete, the evaporation should be continued for at least one hour after the hydrochloric acid has been driven off, as is indicated by the dried salts becoming much more pale in color. Add 10 ml. of concentrated hydrochloric acid, break up any lumps with a polyethylene rod and add 100 ml. of hot water. Allow to stand for 10 minutes to dissolve the salts present. Transfer the silica to a 15-cm. Whatman No. 54 paper, carefully wash out the Teflon dish with (1+20) hydrochloric acid into the filter, wipe the inside surfaces of the dish with a small piece of No. 54 filter paper to remove adhering silica and add the paper to the separated silica. Wash the silica thoroughly with hot dilute hydrochloric acid (1+20) until iron staining is no longer evident. Finally wash once with hot water. Return the filtrate and washings to the Teflon dish and evaporate to dryness as before. Add 5 ml. of concentrated hydrochloric acid, break up the lumps, and add 50 ml. of hot water. Allow to stand for 10 minutes then filter through a fresh 15 cm. Whatman No. 54 paper. Again clean out the dish thoroughly, using small pieces of No. 54 paper to remove adhering silica. Add the small pieces of paper to the silica, then wash with 1 + 20 hydrochloric acid as before, giving a final rinse with hot water. Retain the filtrate and washings. Place the drained but still moist filter papers in an unweighed platinum crucible and heat carefully on a Meker burner to carbonize the papers. Keep the lid on the crucible so that the papers do not burst into flame. Transfer the crucible, without the lid, to a muffle furnace and continue the ignition at 1150–1200° C for one-half hour. Replace the crucible lid after putting the crucible in a desiccator to cool. Weigh the crucible and record the weight as "crucible + silica + X". Moisten the silica residue in the crucible with water and add 5 ml. of hydrofluoric acid followed by a few drops of concentrated sulfuric acid. Mix well with a polyethylene rod, then evaporate slowly to dryness on a hot plate regulated to a low heat so as to avoid boiling. Finally ignite at 1150–1200° C in a muffle furnace for 5 minutes, cool in a desiccator and re-weigh as "crucible + X". The loss in weight represents the amount of silica originally present in the crucible.

The residue "X" remaining in the crucible may contain small amounts of iron and titanium. Recover this residue by adding about 1.0 gram of sodium carbonate and fusing over a Meker burner. When the melt has cooled, dissolve it in a small amount of water and dilute hydrochloric acid (1+1). The solution should be added to the previously retained filtrates and washings, the total volume of which should amount to about 300 ml.

(6) Total Mixed Oxides (Al_2O_3 , TiO_2 , P_2O_5 and Iron as Fe_2O_3)

Add 15 ml. of a 300 gm./litre ammonium chloride solution to the combined filtrate and washings from the silica separation and heat to boiling in a 600 ml. beaker. Add a few drops of methyl red indicator and run concentrated ammonia into the solution from a burette* until the color changes to a distinct yellow. Heat to boiling for 1 or 2 minutes to flocculate the precipitate and if the color changes to orange or red add a few more drops of ammonia to restore the yellow color. If much iron is present the indicator color may be obscured; it is then better to use the indicator externally, on a clean white tile, finally washing the test spots back into the precipitation beaker with distilled water. Without delay, filter the hot solution through a 15 cm. Whatman No. 54 filter paper, washing the beaker and precipitate three or four times with hot 2 per cent ammonium nitrate solution. It is not necessary to remove the precipitate quantitatively from the beaker. Collect the filtrate and washings in a fresh 600 ml. beaker, cover with a watch glass after evaporating down to about 150 ml., and place to one side for later use. Put the original precipitation beaker under the filter and immediately redissolve the precipitate in a minimum amount of hot dilute hydrochloric acid (1 + 1) squirted from a small polyethylene wash bottle. Finally wash the paper a few times with hot water and reserve.

If the precipitate is not redissolved within a few minutes of washing with the ammonium nitrate it will be found that it will become extremely difficult, if not impossible, to redissolve in a reasonable amount of acid. This difficulty appears to increase with the proportion of alumina in the precipitate.

Dilute the solution to about 250 ml., heat to boiling and reprecipitate with ammonia as before. Add 0.5 gm. of Whatman Standard grade ashless cellulose powder, bring to boiling again and filter immediately through the original filter paper, combining the filtrate with the 150 ml. of evaporated filtrate previously set aside. The cellulose powder greatly assists filtration and washing of the precipitate. Use a small piece of No. 54 paper to wipe out all traces of precipitate from the beaker adding it to the precipitate in the filter. Without delay, the precipitate should be well

* Burettes used for analysis should have stopcocks with adjustable greaseless Teflon plugs. The all-glass variety used in old-type burettes is completely unreliable.



Figure 4. Guth washbottles used to refill burettes via 1/8-inch N.B. polyethylene tubing are in a number of ways superior to many of the automatic burettes at present on the market. Alberta Government photograph.

washed with hot 2 per cent ammonium nitrate solution, and finally washed once with hot water, then allowed to drain.

Transfer the filter and precipitate to an accurately weighed platinum crucible, put the lid on the crucible and carbonize the paper at low temperature on a Meker burner. When the paper is completely carbonized, place the crucible and its contents in a muffle furnace at 1150 - 1200°C

for one-half hour. Replace the lid after putting the crucible in a desiccator to cool and weigh as "crucible + total mixed oxides + Y". Reheat the crucible for 10-minute periods until constant weight is attained.

The quantity "Y" represents the small amount of silica (about one milligram) that almost invariably escapes the silica separation procedure but is coprecipitated with the hydrated mixed oxides. This, like the main portion of silica, is determined by volatilization as silicon tetrafluoride: moisten the mixed oxides with water, add a few drops of concentrated hydrofluoric acid (48%) and 2 to 3 ml. of concentrated sulfuric acid. Evaporate slowly to dryness on a hot plate regulated to a low heat, then ignite for 5 minutes at 1150–1200°C in a muffle furnace. Cool in a desiccator and reweigh as "crucible + mixed oxides". The difference "Y" between the last two weighings should be added to the weight of silica determined as in Section (5) above.

(6a) Removal of Manganese

Add 10 ml. of 0.2M sodium sulfide solution to the combined filtrates from operation (6). Add 0.2 gm. of cellulose powder, heat to boiling, then allow to stand for 5 minutes before filtering through a small No. 54 filter paper. Wash the paper and residue with a small amount of water.

(7) Calcium

If the volume of filtrate after the manganese removal is excessive, concentrate to about 250 ml. by evaporation. Add 5 ml. of concentrated hydrochloric acid and heat to boiling. Add a few drops of methyl red indicator and 50 ml. of warm 4 per cent ammonium oxalate solution. While still hot (70–80°), neutralise with concentrated ammonium hydroxide added dropwise until the color changes from red to yellow. Stir the mixture occasionally and allow to stand without further heating for 50 to 60 minutes. Filter through a 15 cm. Whatman No. 40 filter paper. Wash the precipitate about five times with cold water, reserving the filtrate and washings for the determination of magnesium.

Wash the precipitate from the paper into a beaker containing 100 ml. of hot dilute (1 + 10) sulfuric acid. Fold the paper over the rim of the beaker and titrate the solution with 0.1N potassium permanganate while it is still hot, using a 25-ml. burette. When a permanent end-point has been reached, place the filter paper in the solution, stir and continue the titration until the faint pink color persists for 30 seconds. One mole of calcium oxalate corresponds to two equivalents of permanganate.

(8) Magnesium

Add the combined filtrates and washings from the calcium determination to a 500-ml. volumetric flask. Dilute the solution to the mark with

water. Transfer an aliquot of the solution (50 ml. or more depending on magnesium content), to a 500-ml. conical flask. Add 10 ml. of 0.2 M sodium sulfide solution followed by 15 ml. of concentrated ammonium hydroxide. Add 1 ml. of Eriochrome Black T indicator solution (magenta color) and titrate with 0.007M EDTA solution to the end point (blue or blue-grey depending on the nature of the solution being analysed; no red tinge should remain). The indicator blank should be determined and subtracted from the titration. A 25-ml. burette will be found convenient for this determination. One mole of EDTA corresponds to one mole of magnesium.

The EDTA solution consists of 2.5 gm. of disodium dihydrogen ethylene diamine tetra-acetate (Versene) dissolved in 1 litre of distilled water. This should be standardized against 10-ml. aliquots of standard 0.01 M magnesium chloride solution prepared by dissolving 0.84 gm. of pure magnesium carbonate (dried at 110°C) in 1 litre of dilute (1+20) hydrochloric acid.

(9) Preparation of Solution B

Transfer 0.4 gm. of the rock sample to a platinum crucible of about 50 ml. capacity. Add 15 ml. of 48 per cent hydrofluoric acid and 5 ml. of concentrated sulfuric acid. Place the lid on the crucible and digest the mixture overnight on a steam bath. Remove the lid and wash back any splashed material into the crucible with water. Add 1 ml. of concentrated nitric acid and heat the crucible on a hot plate to evaporate the fluoride. Continue heating until strong sulfuric acid fumes are evolved. Cool the crucible and its contents, then add about 30 ml. of water, stir with a polyethylene rod, rinse the rod, replace the lid and digest on the steam bath to dissolve or disperse the residue. Transfer the mixture to a Vycor beaker and dilute to about 100 ml. Boil the mixture gently until the volume has decreased to about 50 ml. If a precipitate remains at this stage remove it by filtration on a small paper, collecting all the filtrate and washings in a 100-ml. volumetric flask. When properly cool, dilute the solution to the mark. This is solution B. Without delay transfer a 25-ml. aliquot of the solution to a polyethylene bottle and reserve for the determination of sodium and potassium.

(10) Total Iron as Fe_2O_3

Add a 5-ml. aliquot of solution B to 5 ml. of 10 per cent hydroxylamine hydrochloride solution contained in a 100-ml. volumetric flask and allow to stand for 10 minutes. Add 10 ml. of 30 per cent sodium citrate solution, then 10 ml. of 0.1 per cent o-phenanthroline solution; dilute to 100 ml., mix, and allow to stand for 1 hour. Compare the absorbance of the solution at a wavelength of 505 m μ with that of standards containing known amounts of iron in the range 0 to 500 μgm Fe_2O_3 .

The standard iron solution may be prepared as follows. Determine the weight per unit length of some degreased pure iron wire of known assay. Cut off a length of this wire calculated to contain about 80 mgm. of iron (0.023-cm. diameter wire weighs approximately 3.25 mgm. per cm.), weigh accurately and trim carefully to exactly 70.0 mgm. Dissolve the wire by warming with 100 ml. water and 10 ml. of dilute (1+1) hydrochloric acid. Transfer the solution to a 2-litre volumetric flask, add a further 10 ml. of 1 + 1 hydrochloric acid and dilute to the mark. This solution contains iron equivalent to exactly 50 $\mu\text{gm. Fe}_2\text{O}_3$ per ml. A standard curve should be prepared using aliquots of 1, 2, 4, 6, 8 and 10 ml. The curve must not be extrapolated upwards: if a sample of high iron-content is encountered, a smaller aliquot should be taken or the solution B should be diluted to stay within the range of the standards.

(11) Titanium

Transfer a 5-ml. aliquot of solution B to a 50-ml. volumetric flask then add, in the following order, 25 ml. of buffer solution, 5 ml. of hydroxybenzene sulfonate reagent and 2 ml. of 20 per cent thioglycolic acid. Mix the contents of the flask by swirling, dilute to the mark with water, mix again and allow to stand for at least 1 hour before measuring the absorbance of the yellow complex at a wavelength of 380 $\text{m}\mu$. The absorbance of a series of solutions should be measured in the same order as their treatment with the reagent, so as to minimise the effect of the very slight further increase with time that continues after one hour's standing. The titanium content is determined by reference to the standard curve which is prepared by pipetting aliquots (0 to 10 ml.) of diluted standard solution into 50-ml. volumetric flasks and processing them in the same way, and at the same time, as the batch of unknown samples.

The buffer solution consists of a mixture of 1 litre of 1.0M sodium acetate solution and 390 ml. of glacial acetic acid. The final pH of the colorimetric solution should be 3.8. The colorimetric reagent is a 5 per cent solution of disodium 1, 2-dihydroxybenzene-3, 5-disulfonate in water; it should be discarded if it develops any slight yellow coloration. Standard titanium solution can be prepared from U.S. National Bureau of Standards titanium dioxide. Heat 0.5 gm. of the dioxide (dried at 110°) with 10 gm. of ammonium sulfate and 25 ml. of concentrated sulfuric acid until it is completely dissolved. Cool the solution, add a further 25 ml. of concentrated sulfuric acid and dilute to 1 litre with distilled water. For colorimetric purposes it is convenient to dilute this further: to a 20-ml. aliquot add 5 ml. of concentrated sulfuric acid and dilute to 1 litre. This provides a solution containing 10 μg of TiO_2 per ml.

(12) Manganese

Pipette a suitable aliquot (up to 20 ml. of solution B or up to 7 ml. of standard manganese solution) into a 50-ml. beaker. If the aliquots taken are less than 20 ml., make up to 20 ml. with distilled water. Add

3 ml. of 85 per cent o-phosphoric acid and 0.2 gm. of potassium periodate. Place cover glasses on the beakers and boil the solutions gently for 10 minutes. Allow to cool, then transfer to 50-ml. volumetric flasks. Dilute the solutions to the mark and compare the absorbance of the sample solution with that of the standards at a wavelength of 528 m μ .

The standard manganese solution is prepared as follows. Pipette 100 ml. of N/10 potassium permanganate solution into a 400-ml. beaker. Add 60 ml. of dilute nitric acid (1 + 1) and add 10 per cent sodium sulfite solution dropwise until the solution is just decolorized. Boil the solution to expell all of the sulfur dioxide, cool, transfer to a 1-litre volumetric flask, and dilute to the mark.

In carrying out this determination, care should be taken to avoid having more than 1.0 mgm. of MnO in the sample aliquot. This corresponds to about 7 ml. of the standard solution.

(13) Phosphorus

Transfer an aliquot (up to 30 ml.) of solution B to a 50-ml. volumetric flask. At the same time pipette aliquots of standard phosphate solution into a series of 50-ml. flasks. The aliquots of standard solution should contain amounts of phosphorus up to about 300 μ g. If the aliquot of standard solution is less than 30 ml., make the volume up to this amount with distilled water. Use a safety pipette to transfer 5 ml. of dilute sulfuric acid (1 + 10) to each of the 50-ml. flasks. Add 5 ml. of 0.25 per cent ammonium meta-vanadate solution (NH_4VO_3) followed by 5 ml. of 5 per cent ammonium molybdate. Mix well after each addition and make up to the mark with distilled water. Mix once more and allow the solutions to stand for 15 minutes before comparing the absorbance of the unknown solution with the absorbance/concentration curve of the standards at a wavelength of 450 m μ .

A suitable standard phosphate solution may be made up from 0.1915 gm. of potassium dihydrogen phosphate (dried at 40°C). Dissolve the phosphate in about 50 ml. of distilled water in a 100-ml. volumetric flask. Add about 2 ml. of dilute nitric acid (1 + 1), mix and dilute to the mark. Make sure that the final solution is well mixed and transfer a 10-ml. aliquot of the solution to a 1-litre volumetric flask. Dilute to the mark with distilled water to obtain a standard solution containing 10.0 μ g P_2O_5 /ml. The diluted standard solution should be kept in a polyethylene container or a Pyrex bottle that has been well leached as a result of having been previously used for the storage of hydrochloric or nitric acid.

(14) Sodium

Sodium is determined by measuring the intensity of its flame emission spectrum with the aid of a Perkin Elmer Flame Photometer, Model 146. Any similar type of instrument would be suitable, although the

method outlined here is intended specifically for the Perkin Elmer instrument. Regardless of the type of instrument to be used, however, the instruction manual supplied with the instrument should first be carefully studied, particularly with regard to the setting up of the instrument and sensitivity adjustment. The instructions given here are for double-beam operation of the Perkin Elmer photometer using an internal lithium standard.

(a) Check the internal standard sensitivity as directed in the instruction manual supplied with the instrument. Return INTERNAL STANDARD control and the COARSE and FINE gain controls to zero.

(b) Increase the COARSE gain sufficiently to enable the ELEMENT SELECTOR to be tuned in accurately to the Na line as judged by the point of maximum meter deflection, while atomising 5 to 10 ml. of a standard solution containing 50 mg. of Na_2O per litre (with or without lithium). Return the COARSE gain to zero.

(c) While atomising 5 to 10 ml. of "zero internal standard" solution containing 100 ppm. Li, adjust the METER knob until the meter reads 50 (null point).

(d) Set INTERNAL STANDARD control for a counter reading of 100.

(e) Atomise the highest Na_2O internal standard solution (50 mg./litre), adjusting the COARSE & FINE gain controls to return the meter needle to the null point.

(f) Set INTERNAL STANDARD to zero counter reading.

(g) Atomise the zero internal standard solution (100 ppm. Li) and, if necessary, readjust METER control knob to return the meter needle to the null point.

(h) Repeat steps (d) to (g) until meter nulls automatically without further gain changes. Record COARSE and FINE settings as a precaution against accidental disturbance and as a check on the consistent operation of the instrument.

(i) Transfer the 25-ml. aliquot of solution B (previously reserved in a polyethylene bottle) to a 100-ml. volumetric flask, add 50 ml. of standard lithium solution containing 200 ppm. Li, dilute to the mark with distilled water and mix well.

(j) While atomising 5 to 10 ml. of this diluted sample solution, adjust the INTERNAL STANDARD dial to return the meter needle to the null point and record the INTERNAL STANDARD dial reading.

(k) Assuming that the dial reading obtained in step (j) is proportional to the Na_2O concentration in the solution (reading of 100 corresponds to 50 mg. Na_2O /litre), calculate the approximate concentration of Na_2O in the diluted sample solution.

(l) While atomising the internal standard Na_2O solution of nearest higher concentration (X_2) to the calculated approximate concentration of Na_2O , adjust the INTERNAL STANDARD dial to return the meter needle to the null point. Record the INTERNAL STANDARD dial reading as Y_2 .

(m) Repeat step (j) and record the INTERNAL STANDARD dial reading as Y .

(n) While atomising the internal standard Na_2O solution of nearest lower concentration (X_1) to the calculated approximate concentration of Na_2O , adjust the INTERNAL STANDARD dial to return the meter needle to the null point. Record the INTERNAL STANDARD dial reading as Y_1 .

(o) Repeat steps (l) (m) and (n).

(p) Using the mean of the two sets of values for Y , Y_1 and Y_2 , calculate the concentration (X) of Na_2O in the original undiluted solution B by substituting in the equation:-

$$X = 4 \left[\frac{(Y - Y_1) (X_2 - X_1)}{(Y_2 - Y_1)} + X_1 \right]$$

The following solutions should be kept available for the flame photometric determination of sodium, and should all be stored in polyethylene bottles.

(a) Stock sodium chloride solution, consisting of 1.886 gm. of dry NaCl in 2 litres of water. This contains 0.5 mg. Na_2O /ml.

(b) Stock lithium sulfate solution, consisting of 184.4 gm. of $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ dissolved in 10 litres of water.

(c) Standard lithium solution, prepared by diluting 200 ml. of the stock solution to 2 litres. This solution contains 200 ppm. Li.

(d) Internal standard sodium solutions, made by adding 0 (zero internal standard), 5, 10, 20, 40, 60, 80 and 100 ml. of stock sodium chloride to 50 ml. of stock lithium sulfate solution and diluting to 1 litre with distilled water. These solutions all contain 100 ppm. Li and amounts of Na_2O ranging from zero to 50 mg. per litre.

(15) Potassium

The procedure for the determination of potassium is exactly the same as for sodium except that the instrument must be tuned in to the potassium line and internal standard potassium solutions must be used.

Additional requirements are:

(a) Stock potassium chloride solution, consisting of 1.584 gm. of dry KCl in 2 litres of water. This contains 0.5 mg. K_2O /ml.

(b) Internal standard potassium solutions, made by adding 0 (zero internal standard) 5, 10, 20, 40, 60, 80 and 100 ml. of stock potassium chloride to 50 ml. of stock lithium sulfate solution and diluting to 1 litre with distilled water. These solutions should all be stored in polyethylene containers.

(16) Ferrous Iron

On account of the great care necessary in this determination (Kolthoff and Sandell, 1943), samples should be processed only one at a time. Fill a 1-litre flask half full of distilled water and boil for several minutes to expel dissolved oxygen. Cool the flask under the cold-water tap immediately prior to carrying out the analysis. Weigh 0.5 gm. of sample into a 30- or 40-ml. platinum crucible which must have a well-fitting cover. Moisten the weighed sample with 1 or 2 ml. of boiled water. In another platinum crucible prepare a mixture of 5 ml. of boiled water and 5 ml. of concentrated sulfuric acid. Add 5 ml. of 48 per cent hydrofluoric acid to the mixture, and stir with a polyethylene rod. Place the crucible containing the sample onto a refractory triangle ready for heating. Pour in the acid mixture from the second crucible and immediately place the cover in position to prevent the ingress of atmospheric oxygen. Heat the sides of the crucible without delay, using a small flame, until steam begins to emerge, then turn down the flame and place the burner directly beneath the crucible so as to keep the solution boiling very gently for 10 minutes. The boiling must proceed uninterruptedly and it may be necessary to protect the flame from drafts in order to achieve this.

While the sample is being decomposed add 200 ml. of the boiled water, 50 ml. of saturated boric acid solution, and 5 ml. of concentrated sulfuric acid to a 600-ml. beaker. By means of tongs (which must not be made of ferrous metal) quickly immerse the crucible, with the cover still in place, in the boric acid solution. Stir the liquid to distribute the contents of the crucible throughout the solution and immediately titrate with 0.1N standard potassium permanganate, while continuing to stir, until the faint pink colour persists for 30 seconds. One equivalent of permanganate corresponds to one mole of FeO .

(17) Ferric Iron

When FeO is found in a sample, the percentage of Fe_2O_3 equivalent to the FeO must be subtracted from the percentage of total iron (Section (10) above) to yield the percentage of ferric iron in the sample.

(18) Aluminum

The aluminum is not determined directly, but is calculated from the weight of "total mixed oxides" by subtracting the corresponding weights of iron oxides (total, as Fe_2O_3), titanium dioxide, and phosphorus pentoxide which have been determined according to sections (10), (11) and (13) above.

METHOD OF REPORTING RESULTS

The results of silicate-rock analyses are usually given in terms of the appropriate acidic or basic oxide radicals, and it has become the accepted practice to list the constituents in the order of their general petrological significance: SiO_2 , Al_2O_3 , Fe_2O_3 , FeO, MgO, CaO, Na_2O , K_2O , loss on ignition, H_2O - ($<110^\circ$), TiO_2 , P_2O_5 , MnO (Total 100%).

This is essentially the order of abundance of the corresponding elements in the earth's crust (cf. Table 1) but certain rearrangements have been made in order to show up the inter-relationship of the acidic and basic constituents more clearly. The results are reported on a percentage basis, to two places of decimals, so that addition to 100 per cent may be used as a check on the analysis. The validity of this check will be discussed below.

POSSIBLE ERRORS AND LIMITATIONS OF THE PRESENT

ANALYTICAL SYSTEM

(a) SiO_2

According to Schlecht & Stevens (Fairbairn, et al., 1951), double dehydration with HCl and recovery of silica from the ignited total mixed oxides should account for practically all of the silica present in the sample. Small negative errors occur more frequently than positive errors and are most likely due to failure to remove all of the tightly adhering silica from the surface of porcelain evaporating dishes, or failure to bake adequately during the second dehydration. The Teflon dishes recommended above greatly reduce the chance of such errors, as their surfaces are not wetted by the solutions and the silica does not adhere to them.

(b) Al_2O_3

Since Al_2O_3 is calculated by subtracting the values for TiO_2 , P_2O_5 , and total iron as Fe_2O_3 , from the total mixed oxides, a gross error in determining these constituents will invalidate the Al_2O_3 figure. In the absence of gross errors, the Al_2O_3 figure will still be subject to an error equal to the square root of the sum of the squares of the errors of the other four determined quantities:- TiO_2 , P_2O_5 , Fe_2O_3 and the total itself. Non-determined minor constituents such as Cr_2O_3 and V_2O_3 will be counted as Al_2O_3 thus it is apparent that the Al_2O_3 determination will be less accurate than any of the other determinations.

(c) Fe_2O_3

Fe_2O_3 is calculated by subtracting the Fe_2O_3 equivalent of the FeO content from the total iron determined as Fe_2O_3 . A gross error in either the total iron or ferrous determination will invalidate the Fe_2O_3 figure. The latter will in any case be subject to an error equal to the square root of the sum of the squares of the errors in the total iron and ferrous iron determinations. In the present analytical system, the method used for total iron is known to be very reliable and particularly free from interferences (Fortune and Mellon, 1938). On the other hand, the ferrous iron determination requires considerable care if reliable results are to be obtained. Note that the absolute error in the ferrous determination increases by a factor of 1.11 in the course of calculating the Fe_2O_3 in the above manner.

(d) FeO

The determination of FeO is subject to at least one major difficulty which may result in low precision even when the nature of the sample itself is ideal. This results from the use of hydrofluoric acid to dissolve the sample. The thermodynamic activity of the ferric ions is so greatly reduced by the formation of the ferric fluoride complex FeF_6^{3-} that the ferrous ions become very easily oxidised by any atmospheric oxygen that may get into the solutions during dissolution of the sample. The procedure given in section (16) above has been designed to minimize oxidation due to this cause. The purpose of the boric acid is to complex the fluoride ions as fluoroboric acid so that the solution may be eventually titrated in the presence of air without much risk of autoxidation.

A further difficulty in the determination can arise in the crushing and grinding of the sample. Some ferrous minerals are apparently easily oxidised in the finely ground state and errors from this source are virtually unavoidable. Some authorities advocate that the rock sample should be ground under alcohol to prevent the access of oxygen, but it is known that grinding produces local high temperatures in the material and that ferric ions can be readily reduced in thermal and photo-chemical reactions with

alcohol. It would therefore appear that in cases where grinding under a liquid is preferred, water or carbon tetrachloride should be used. The apparently greater efficiency of alcohol, in spite of its greater solvent power for oxygen, in "preventing oxidation" during grinding (Hillebrand and Lundell, 1953) is probably due to actual reduction of some of the ferric iron.

The presence of organic matter or sulfur in the sample can cause serious errors in the determination of the ferrous oxide content. If present in the sulfide form, one atom of sulfur could theoretically reduce three molecules of ferric oxide to the ferrous state in the course of its oxidation to sulfur dioxide. In terms of percentages, 0.10 per cent of sulfur could produce a positive error of 1.35 per cent in the FeO determination. Elementary carbon, because of its smaller atomic weight, could have an even greater effect, thus 0.1 per cent carbon could produce a positive error of 2.4 per cent in the FeO determination. It should be borne in mind that the analytically determined ferrous:ferric ratio is extremely prone to errors due to carbon and sulfur, especially when the ferric content is high and the ferrous content is low.

(e) MgO

Any calcium not precipitated during the oxalate precipitation will be titrated as magnesium, 1.0 per cent of calcium oxide being equivalent to 0.72 per cent magnesium oxide. If the removal of manganese by the procedure described in section (6a) above is incomplete, some trouble may be experienced due to catalyzed oxidation of the Eriochrome Black T indicator dye. This imparts a reddish brown tinge to the solution and obscures the end point.

(f) CaO

The most likely error to arise in the calcium determination as described in section (7) above is due to co-precipitation of magnesium oxalate; 1.0 per cent of MgO would be reported as 1.39 per cent CaO. However, if the directions in section (7) are carefully followed, the extent of such co-precipitation will be negligible so far as routine analyses are concerned (Kolthoff and Sandell, 1943). Strontium will be precipitated with the calcium, but is regarded as only a minor constituent of silicate rocks; 0.1 per cent of SrO would be reported as 0.054 per cent CaO.

(g) Na₂O

The flame-photometric method used in the present analytical method does not appear to be subject to any inherent errors other than those arising from instrumental and personal sources.

(h) K_2O

The flame-photometric method is particularly suited to the determination of potassium oxide, and the same remarks apply as in the sodium oxide case.

(i) Loss on ignition

The actual weight loss on ignition at a temperature of 1150–1200°C can be determined with high accuracy. However, the interpretation of the weight loss is subject to a number of uncertainties. Generally the weight loss is attributed to H_2O and CO_2 , but one other additional factor usually has to be taken into consideration. Thus, if FeO is present in the sample it will become oxidised to Fe_2O_3 causing the weight loss on ignition to be less than it would otherwise be. This effect may be allowed for as explained in section (3) above. Of the other major constituents of silicate rocks, only changes in the state of combination of manganese give rise to any uncertainty regarding the significance of the ignition loss, but generally only very small amounts of manganese are present in rock samples so that it is reasonably safe to ignore such effects. The minor constituents S, F and Cl may slightly increase this uncertainty, since sulfur may be driven off as oxides of sulfur from sulfates or sulfides while some loss of HCl may result from hydrolysis of chlorides. The presence of fluoride in the sample may give rise to the evolution of traces of SiF_4 .

(j) H_2O

The actual weight loss on drying a sample at 110°C can be determined very accurately as can the loss on ignition but, once again, there is some uncertainty regarding the interpretation of the weight loss. The latter may be affected by the grinding and storage conditions to which the sample is subjected. For example, fine grinding may permit the escape of some water or, on the other hand, may expose a large surface which can adsorb atmospheric water vapour. To minimize uncertainties from these sources it is best to adhere strictly to some standard procedure for sample preparation and storage.

(k) TiO_2

The method used for titanium determination has been discussed previously in detail (Rigg and Wagenbauer, 1961), and has been found to be rapid, sensitive and free from interferences by other major rock constituents. The only errors likely to arise are instrumental and personal.

(l) P_2O_5

The method given above in section (13) is based on the recommendations of Quinlan and DeSesa (1955) who critically investigated all

aspects of the spectrophotometric determination of phosphorus as molybdovanadophosphoric acid. High results may be obtained unless care is taken to ensure that all the silica is volatilized during the preparation of the solution B. Gross amounts of ferric iron also cause a positive error but at the wavelength suggested in the present work (450 mμ) interference from the amount of iron encountered in silicate rock samples will be negligible. If very little iron is present in the sample a considerable increase in sensitivity may be achieved by using a wavelength of 400 mμ (Jackson, 1958). This particular method is not very sensitive to the acidity (H_2SO_4) of the sample. It has been found, for instance, that the equivalent of 1 ml. of concentrated sulfuric acid may be present in the sample aliquot used without causing any error. Ferric ions can be tolerated to the extent of 20 mg. Fe in the sample aliquot. Although it has been suggested (Jackson, 1958) that this method is adaptable to nitric acid systems, it has been found that the use of 5 ml. of dilute nitric acid (1+1) in place of the 5 ml. of dilute sulfuric acid (1+10) renders this analysis very prone to serious negative errors when the sample contains up to the equivalent of 1 ml. of concentrated sulfuric acid. If neutralization with ammonia or sodium hydroxide is attempted prior to processing the aliquot, the errors become positive.

(m) MnO

In the absence of chlorides, bromides and carbonaceous matter from the solution B (which will normally be the case) the periodate method described in section (12) above is highly specific and free from interference.

(n) Summation to 100 per cent

As pointed out by Schlecht and Stevens (Fairbairn et al., 1951) the traditional practice of inspecting the summation of a rock analysis is a necessary test of its correctness, but a summation close to 100.00 per cent does not necessarily guarantee correctness. This arises from the fact that many of the possible errors are self-compensating to a certain extent, especially where exclusively gravimetric methods are used. It should be noted that the analytical system described above is more sensitive than most to apparently poor summations: for example, any silica or aluminum remaining in the filtrates from the R_2O_3 separation will escape possible reweighing completely since no further gravimetric procedures are used after this stage.

EVALUATION OF THE ANALYTICAL SYSTEM

After proving out the various individual methods against standard samples, the whole analytical system described above was tested on two standard rock samples obtained from the Analytical Laboratories Branch of the U.S. Geological Survey. The samples were granite G-1 and diabase W-1. The results for G-1 are shown in table 2; those for W-1 are shown in table 3. Each sample was analyzed four times (columns A, B, C and D),

the analyst being aware that there were four sets of two samples but not knowing the actual identity of the samples. The results of each of the four runs is shown for both samples and the mean values are compared with the mean values reported by Stevens et al. (1960). The number of determinations (n) taken into consideration in Stevens' publication is also shown in tables 2 and 3 together with the standard deviations. The standard deviation (s) is defined as $\sqrt{\frac{d^2}{n-1}}$ where d is the deviation of the result from the mean (\bar{x}) of n determinations.

On the basis of the arbitrarily adopted limits of acceptability ($\bar{x} \pm s$) used by Stevens et al. (1960), it can be seen in the case of the Research Council laboratory mean results for G-1 that the SiO_2 and Fe_2O_3 figures would be considered too low and the MgO figure too high. On the same basis the figure for CaO reported for W-1 is too high.

The "loss on ignition corrected for FeO " determined in the Research Council laboratory is within the limits set for CO_2 and $\text{H}_2\text{O}+$ combined in the case of the U.S. Geological Survey results for G-1 and W-1.

If the limits of acceptability are defined by $\bar{x} (\pm) 2s$ as used earlier by Fairbairn et al. (1951) only 1 of the 120 individual determinations reported by the Research Council laboratory in tables 2 and 3 would be considered "unacceptable": this is the SiO_2 value reported for G-1 sample A.

It is reported by Fairbairn et al. (1951), that even if one "unacceptable" determination is allowed each of the 25 co-operating laboratories, less than two thirds of these laboratories pass for all determinations. When it is considered that the methods used in the laboratories taking part in the U.S. Geological Survey co-operative investigation are presumably those thought to provide the greatest accuracy, whereas the Research Council system has been deliberately designed to offer a reasonable compromise between speed and accuracy, it is apparent that use of the latter system is well justified for routine analysis of silicate rocks for general geological purposes.

Table 2. Results of Analysis of U.S. Geological Survey Sample G-1

| Constituent | R.C.A. Analytical Report 62/19 | | | | | U.S.G.S. Bulletin 1113 | | |
|--|--------------------------------|-------|-------|-------|-------|------------------------|--------------------|-----|
| | A | B | C | D | Mean | Mean | Standard deviation | n |
| SiO ₂ | 71.26 | 71.80 | 71.86 | 71.86 | 71.70 | 72.35 | 0.48 | 60 |
| Al ₂ O ₃ | 14.34 | 14.12 | 14.35 | 14.29 | 14.28 | 14.32 | 0.37 | 60 |
| Fe ₂ O ₃ | 0.49 | 0.61 | 0.65 | 0.68 | 0.61 | 0.95 | 0.30 | 57 |
| FeO | 1.15 | 1.08 | 1.08 | 1.08 | 1.10 | 0.99 | 0.11 | 57 |
| MgO | 0.58 | 0.65 | 0.64 | 0.55 | 0.61 | 0.40 | 0.13 | 59 |
| CaO | 1.43 | 1.50 | 1.46 | 1.46 | 1.46 | 1.40 | 0.12 | 59 |
| Na ₂ O | 3.37 | 3.42 | 3.32 | 3.33 | 3.36 | 3.31 | 0.23 | 59 |
| K ₂ O | 5.15 | 5.25 | 5.19 | 5.19 | 5.20 | 5.42 | 0.39 | 59 |
| H ₂ O - | 0.07 | 0.06 | 0.05 | 0.05 | 0.06 | 0.06 | 0.05 | 48 |
| H ₂ O+ | --- | --- | --- | --- | --- | 0.36 | 0.18 | 51 |
| TiO ₂ | 0.25 | 0.25 | 0.25 | 0.25 | 0.25 | 0.26 | 0.04 | 60 |
| P ₂ O ₅ | 0.16 | 0.14 | 0.15 | 0.17 | 0.16 | 0.10 | 0.06 | 54 |
| MnO | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.03 | 0.01 | 56 |
| CO ₂ | --- | --- | --- | --- | --- | 0.08 | 0.01 | 9 |
| Loss on ignition corrected for FeO | 0.53 | 0.53 | 0.54 | 0.62 | 0.55 | --- | --- | --- |
| Total | 98.82 | 99.45 | 99.58 | 99.57 | 99.38 | 100.03 | --- | --- |
| Total Fe as Fe ₂ O ₃ | 1.77 | 1.81 | 1.85 | 1.88 | 1.83 | 2.04 | 0.28 | 60 |
| Total mixed oxides | 16.52 | 16.32 | 16.60 | 16.49 | 16.48 | 16.72 | 0.40 | 60 |

Table 3. Results of Analysis of U. S. Geological Survey Sample W-1

| Constituent | R. C. A. Analytical Report 62/19 | | | | | U. S. G. S. Bulletin 1113 | | |
|--|----------------------------------|--------|--------|--------|--------|---------------------------|--------------------|-----|
| | A | B | C | D | Mean | Mean | Standard deviation | n |
| SiO ₂ | 52.52 | 52.41 | 52.50 | 53.25 | 52.67 | 52.40 | 0.33 | 60 |
| Al ₂ O ₃ | 15.19 | 15.06 | 15.25 | 15.23 | 15.18 | 15.11 | 0.63 | 60 |
| Fe ₂ O ₃ | 0.93 | 1.11 | 1.18 | 1.10 | 1.08 | 1.62 | 0.71 | 58 |
| FeO | 8.98 | 8.91 | 8.85 | 8.91 | 8.91 | 8.63 | 0.41 | 58 |
| MgO | 6.92 | 6.86 | 6.81 | 6.92 | 6.88 | 6.58 | 0.35 | 59 |
| CaO | 11.19 | 11.19 | 11.16 | 11.22 | 11.19 | 10.97 | 0.16 | 59 |
| Na ₂ O | 2.17 | 2.11 | 2.16 | 2.15 | 2.15 | 2.07 | 0.20 | 58 |
| K ₂ O | 0.56 | 0.57 | 0.56 | 0.56 | 0.56 | 0.67 | 0.13 | 58 |
| H ₂ O - | 0.16 | 0.16 | 0.17 | 0.14 | 0.16 | 0.16 | 0.06 | 54 |
| H ₂ O + | --- | --- | --- | --- | --- | 0.54 | 0.20 | 55 |
| TiO ₂ | 1.06 | 1.07 | 1.04 | 1.00 | 1.04 | 1.07 | 0.20 | 60 |
| P ₂ O ₅ | 0.14 | 0.16 | 0.11 | 0.10 | 0.13 | 0.15 | 0.06 | 58 |
| MnO | 0.18 | 0.18 | 0.18 | 0.18 | 0.18 | 0.17 | 0.05 | 59 |
| CO ₂ | --- | --- | --- | --- | --- | 0.06 | 0.03 | 10 |
| Loss on ignition corrected for FeO | 0.79 | 0.82 | 0.80 | 0.85 | 0.82 | --- | --- | --- |
| Total | 100.79 | 100.61 | 100.77 | 101.61 | 100.95 | 100.20 | --- | --- |
| Total Fe as Fe ₂ O ₃ | 10.91 | 11.01 | 11.01 | 11.00 | 10.98 | 11.22 | 0.28 | 60 |
| Total mixed oxides | 27.30 | 27.30 | 27.41 | 27.33 | 27.34 | 27.54 | 0.48 | 60 |

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APPENDIX

Reagents Required

(Concentrations of reagents are given in per cent W/V, except where stated otherwise. Those marked with an asterisk should be used only when fresh.)

Acetate buffer solution (1 litre of 1.0M sodium acetate solution mixed with 390 ml. of glacial acetic acid)

Ammonium chloride solution, 300 grams/litre

Ammonium hydroxide, S.G. = 0.90

Ammonium metavanadate solution, 0.25%

Ammonium molybdate solution, 5%

Ammonium nitrate solution, 2%

Ammonium oxalate solution, 4%

Ammonium sulfate

Boric acid solution, saturated

* Disodium 1, 2 - dihydroxybenzene - 3, 5 - disulphonate solution, 5%

EDTA, 0.007M Standardized solution (2.5 grams of disodium dihydrogen ethylene diamine tetra-acetate/litre).

* Eriochrome Black T indicator solution, 0.1%, filtered

Hydrochloric acid, concentrated

Hydrochloric acid, dilute, 1 + 1

Hydrochloric acid, dilute, 1 + 20

Hydrofluoric acid, 48% w/w

Hydroxylamine hydrochloride solution, 10%

Iron wire, pure, assayed, 0.023 cm. diameter

Lithium sulfate

Reagents Required (Continued)

Magnesium carbonate

Methyl red indicator, alcoholic solution, 0.02%

Nitric acid, concentrated

Nitric acid, dilute, 1+1

* o-Phenanthroline solution, 0.1%

o-Phosphoric acid, 85% w/w

Potassium Chloride

Potassium dihydrogen phosphate

Potassium periodate

Potassium permanganate, 0.1N standardised solution

Sodium carbonate, anhydrous

Sodium chloride

Sodium citrate solution, 30%

Sodium hydroxide solution, 5%

Sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$) solution, 5%

Sodium sulfite solution, 10%

Sulfuric acid, concentrated

Sulfuric acid, dilute, 1 + 10

* Thioglycolic acid solution, 20% v/v

Titanium dioxide, National Bureau of Standards

Other Requirements

Cellulose powder

Filter papers

Universal indicator paper

N.L.C. - B.N.C.



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